

# Anomalous physical properties of underdoped weak-ferromagnetic superconductor $\text{RuSr}_2\text{EuCu}_2\text{O}_8$

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Similar to the optimal-doped, weak-ferromagnetic (WFM induced by canted antiferromagnetism,  $T_{\text{Curie}} = 131$  K) and superconducting ( $T_c = 56$  K)  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ , the underdoped  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$  ( $T_{\text{Curie}} = 133$  K,  $T_c = 36$  K) also exhibited a spontaneous vortex state (SVS) between 16 K and 36 K. The low field ( $\pm 20$  G) superconducting hysteresis loop indicates a weak and narrow Meissner state region of average lower critical field  $B_{\text{cl}}^{\text{ave}}(T) = B_{\text{cl}}^{\text{ave}}(0)[1 - (T/T_{\text{SVS}})^2]$ , with  $B_{\text{cl}}^{\text{ave}}(0) = 7$  G and  $T_{\text{SVS}} = 16$  K. The vortex melting transition ( $T_{\text{melting}} = 21$  K) below  $T_c$  obtained from the broad resistivity drop and the onset of diamagnetic signal indicates a vortex liquid region due to the coexistence and interplay between superconductivity and WFM order. No visible jump in specific heat was observed near  $T_c$  for Eu- and Gd-compound. This is not surprising, since the electronic specific heat is easily overshadowed by the large phonon and weak-ferromagnetic contributions. Furthermore, a broad resistivity transition due to low vortex melting temperature would also lead to a correspondingly reduced height of any specific heat jump. Finally, with the baseline from the nonmagnetic Eu-compound, specific heat data analysis confirms the magnetic entropy associated with antiferromagnetic ordering of  $\text{Gd}^{3+}$  ( $J = S = 7/2$ ) at 2.5 K to be close to  $N_A k \ln 8$  as expected.

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## I. INTRODUCTION

Anomalous physical properties have been observed recently in the weak-ferromagnetic (WFM induced by canted antiferromagnetism) and high- $T_c$  superconducting  $\text{RuSr}_2\text{RCu}_2\text{O}_8$  system (Ru-1212 with  $R = \text{Sm}$ ,  $\text{Eu}$ ,  $\text{Gd}$ , and  $\text{Y}$ ) having a tetragonal  $\text{TiBa}_2\text{CaCu}_2\text{O}_7$ -type structure.<sup>1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51</sup> Possible superconductivity was also reported in Ca-substituted WFM compounds  $\text{RuCa}_2\text{RCu}_2\text{O}_8$  ( $R = \text{Pr}$ - $\text{Gd}$ ).<sup>49,50,51</sup> The weak-ferromagnetism in these strongly-correlated electron systems originates from the long range order of Ru moments in the  $\text{RuO}_6$  octahedra due to a strong  $\text{Ru-4}d_{xy,yz,zx}\text{-O-2}p_{x,y,z}$  hybridization with a Curie temperature  $T_{\text{Curie}} \sim 131$  K. A G-type antiferromagnetic order probably occurs with  $\text{Ru}^{5+}$  moment  $\mu$  canted along the tetragonal basal plane, even through the small net spontaneous magnetic moment  $\mu_s \ll \mu(\text{Ru}^{5+})$  is too small to be detected in neutron diffraction.<sup>4,5,9,10,22</sup> The Ru valence of 4+ and 5+ was determined from x-ray absorption near edge measurements.<sup>23,52</sup>

With its quasi-two-dimensional  $\text{CuO}_2$  bi-layers separated by a rare earth layer in the Ru-1212 structure,  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  has the highest resistivity-onset temperature  $T_c \sim 60$  K among different Ru-1212

compounds.<sup>1,2,4,5,31</sup> A broad resistivity transition width  $\Delta T_c = T_c(\text{onset}) - T_c(\text{zero}) = T_c - T_{\text{melting}} \sim 15\text{-}20$  K is most likely a consequence of coexistence and interplay between superconductivity and WFM order. The diamagnetic signal is observed only near  $T_{\text{melting}}$  instead of  $T_c$ , and a reasonable large Meissner signal can be detected only in zero-field-cooled (ZFC) mode.<sup>47</sup> Lower  $T_c > 40$  K and 12 K were observed for Eu-compound and Sm-compound, respectively.<sup>12,18</sup> No superconductivity can be detected in  $\text{RuSr}_2\text{RCu}_2\text{O}_8$  ( $R = \text{Pr}$ ,  $\text{Nd}$ ),<sup>3,16</sup> while a superconducting  $\text{RuSr}_2\text{YCu}_2\text{O}_8$  phase is stable only under the high pressure.<sup>21,26</sup>

Interest of the current work stimulates from a recent report of spontaneous vortex state (SVS) between 30 K and 56 K in  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ .<sup>47</sup> However, the compound undergoes a low temperature antiferromagnetic ordering arising from  $\text{Gd}^{3+}$  at 2.5 K. To avoid this complication, isostructural  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$  with nonmagnetic- $\text{Eu}^{3+}$  ions was chosen as a prototype material in this study to evaluate the anomalous magnetic, transport, calorimetric properties and  $d$ -wave nature near and below  $T_c = 36$  K. The calorimetric data were further used as a basis in elucidating the magnetic entropy associated with the  $\text{Gd}^{3+}$  ordering.

## II. EXPERIMENTAL

Stoichiometric  $\text{RuSr}_2\text{RCu}_2\text{O}_8$  samples were synthesized by solid-state reactions. High-purity  $\text{RuO}_2$  (99.99 %),  $\text{SrCO}_3$  (99.9 %),  $\text{R}_2\text{O}_3$  (99.99 %) ( $\text{R} = \text{Pr}$ ,  $\text{Nd}$ ,  $\text{Sm}$ ,  $\text{Eu}$ , and  $\text{Gd}$ ), and  $\text{CuO}$  (99.9 %), in the nominal composition ratios of  $\text{Ru}:\text{Sr}:\text{R}:\text{Cu} = 1:2:1:2$ , were well mixed and calcined at  $960^\circ\text{C}$  in air for 16 hours. The calcined powders were then pressed into pellets and sintered in flowing  $\text{N}_2$  gas at  $1015^\circ\text{C}$  for 10 hours to form  $\text{RuSr}_2\text{RO}_6$  and  $\text{Cu}_2\text{O}$  precursors. This step is crucial in order to avoid the formation of impurity phases. The  $\text{N}_2$ -sintered pellets were heated at  $1060^\circ\text{C}$  in flowing  $\text{O}_2$  gas for 10 hours to form the Ru-1212 phase, then oxygen-annealed at a slightly higher  $1065^\circ\text{C}$  for 7 days and slowly furnace-cooled to room temperature with a rate of  $15^\circ\text{C}$  per hour.<sup>47</sup>

Powder x-ray diffraction data were collected with a Rigaku Rotaflex 18-kW rotating-anode diffractometer using  $\text{Cu-K}\alpha$  radiation. Four-probe electrical resistivity measurements were performed with a Linear Research LR-700 ac (16Hz) resistance bridge from 2 K to 300 K. Magnetic susceptibility and magnetic hysteresis measurements from 2 K to 300 K in low applied magnetic fields were carried out with a Quantum Design  $\mu$ -metal shielded MPMS2 superconducting quantum interference device (SQUID) magnetometer. Calorimetric measurements were made from 1 K to 70 K by using a thermal-relaxation microcalorimeter. A mg-size sample was attached with a minute amount of grease to a sapphire holder to ensure good thermal coupling. The sample holder had a Cernox temperature sensor and a Ni-Cr alloy film heater. The holder was linked thermally to a copper block by four Au-Cu alloy wires. The temperature of the block could be raised in steps but held constant when a heat pulse was applied. Following each heat pulse, the sample temperature relaxation rate was monitored to yield a time constant  $\tau$ . The total heat capacity was calculated from the expression  $c = \kappa\tau$ , where  $\kappa$  is the thermal conductance of Au-Cu wires. The heat capacity of the holder was measured separately for addenda correction. The molar specific heat of the sample was then obtained from  $C = (c - c_{\text{addenda}})/(\text{m}/\text{M})$  with  $\text{m}$  and  $\text{M}$  being the sample's mass and molar mass, respectively.

## III. RESULTS AND DISCUSSION

Figure 1 summarizes structural and superconducting properties, as a function of  $\text{R}^{3+}$  ionic radius  $r$  (coordination number  $\text{CN} = 8$ ), of various  $\text{RuSr}_2\text{RCu}_2\text{O}_{8-\delta}$  system ( $\text{R} = \text{Pr}$ - $\text{Y}$ ).  $T_c$  decreases from a maximum value of 60 K for optimal-doped Gd ( $r = 0.105$  nm) to 36 K for underdoped Eu ( $r = 0.107$  nm), and  $< 10$  K for Sm ( $r = 0.108$  nm). Larger rare earth ions of Nd (0.112 nm) and Pr (0.113 nm) lead to a metal-insulator transition. Powder x-ray Rietveld refinement study indicates that the insulating phase is stabilized in the undistorted tetrag-

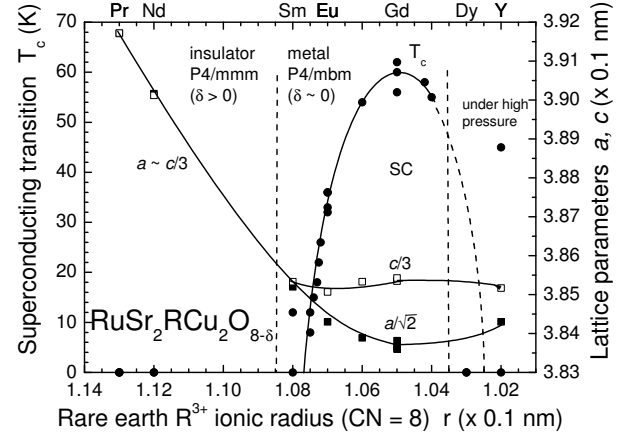


FIG. 1: The variation of superconducting transition  $T_c$  and tetragonal lattice parameters  $a$ ,  $c$  with rare earth ionic radius  $\text{R}^{3+}$  (coordination number  $\text{CN} = 8$ ) for  $\text{RuSr}_2\text{RCu}_2\text{O}_{8-\delta}$  system ( $\text{R} = \text{Pr}$ - $\text{Y}$ ).

onal phase (space group  $\text{P4/mmm}$ ) with a larger lattice parameter  $a \sim 0.390$ - $0.392$  nm, which gives a reasonable  $\text{Ru}^{5+}$ -O bond length of  $d \sim 0.197$  nm if the oxygen content is slightly deficient ( $\delta > 0$ ). On the other hand, the metallic phase with smaller rare earth ions can be stabilized in the full-oxygenated ( $\delta \sim 0$ ), distorted tetragonal phase (space group  $\text{P4/mbm}$ ) with smaller  $a/\sqrt{2} \sim 0.383$ - $0.385$  nm but still a reasonable Ru-O bond length through  $\text{RuO}_6$  octahedron rotation.

Indeed, the powder x-ray diffraction pattern for the oxygen-annealed  $\text{RuSr}_2\text{EuCu}_2\text{O}_{8-\delta}$  sample indicates single phase with tetragonal lattice parameters of  $a = 0.5435(5)$  nm and  $c = 1.1552(9)$  nm. A Raman scattering peak of  $265 \text{ cm}^{-1}$  indicates that the  $\text{A}_{1g}$  mode symmetry belong to a  $\text{P4/mbm}$  instead of  $\text{P4/mmm}$  group. Accordingly, with  $\text{RuO}_6$  octahedra rotation angle  $\theta \sim 14^\circ$  around the  $c$ -axis and oxygen parameter  $\delta \sim 0$ ,<sup>10</sup> Rietveld refinement analysis with a small residual error factor  $R = 5.31\%$  yields a reasonable Ru-O bond lengths  $d = (a/2\sqrt{2})(1 - \sin^2\theta)^{-1/2} = 0.198$  nm. It is close to the minimum calculated bond length  $d(\text{Ru}^{5+}\text{-O})$  of  $0.197$  nm.<sup>10</sup>

Figure 2 shows the temperature dependence of field-cooled (FC) and zero-field-cooled (ZFC) volume magnetic susceptibility  $4\pi\chi_V$  at 1-G for bulk and powder  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$  samples. Weak-ferromagnetic ordering occurs at  $T_{\text{Curie}} = 133$  K. Similar to  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ ,<sup>47</sup> this Eu-compound has its electrical resistivity data, which are also included in Fig. 2, exhibiting a non-Fermi-liquid-like behavior above  $T_{\text{Curie}}$ . The linearly temperature-dependant values of  $10.0 \text{ m}\Omega \text{ cm}$  at 300 K and  $5.5 \text{ m}\Omega \text{ cm}$  at 160 K give an extrapolated value of  $2.6 \text{ m}\Omega \text{ cm}$  at 0 K, yielding a ratio  $\rho(300 \text{ K})/\rho(0 \text{ K})$  of 3.9. Below  $T_{\text{Curie}}$ , a  $T^2$  behavior prevails. The onset of deviation at 36 K from such a temperature dependence is taken as the superconducting transition temperature  $T_c$ . The melting temperature of superconducting vortex

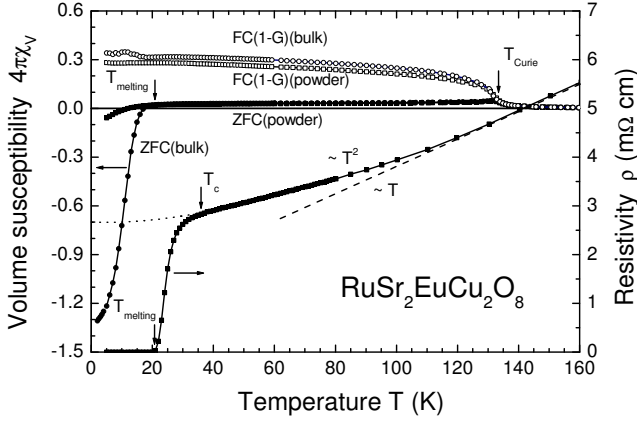


FIG. 2: The electrical resistivity  $\rho(T)$  and volume magnetic susceptibility  $4\pi\chi_V(T)$  in 1-G field-cooled (FC) and zero-field-cooled (ZFC) modes for oxygen-annealed bulk and powder  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$  samples.

liquid is assigned to  $T_{\text{melting}} = 21$  K, where resistivity reaches zero.<sup>47</sup> The broad transition width of 15 K is the common feature for all reported Ru-1212 compounds. It indicates that the superconducting Josephson coupling along the tetragonal  $c$ -axis between Cu-O bi-layers may be partially blocked by the magnetic dipole field  $B_{\text{dipole}}$  of ordered Ru moments in the Ru-O layer.<sup>47</sup>

The Meissner shielding at 2 K is complete ( $4\pi\chi_V = 4\pi M/B_a \sim 1.3$ ) for ZFC bulk sample, but much reduced (-0.1) in the powder sample. However, in 1-G FC mode, no such an effect can be detected below  $T_{\text{melting}}$  due to strong flux pinning.

Low-field ( $\pm 20$  G) superconducting hysteresis loop at 2 K for bulk sample  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$  and  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  as reference are shown in Fig. 3. The initial magnetization curve deviates from straight line at 2 G and 3 G for the Eu- and Gd-compound, respectively. The narrow region of full Meissner effect roughly reflects the temperature-dependent lower critical field in the  $ab$ -plane  $B_{c1}^{ab}(T)$ . The average lower critical field  $B_{c1}^{ave}$  for bulk sample as determined from the peak of initial diamagnetic magnetization curves is 7 G for  $R = \text{Eu}$  and 13 G for  $R = \text{Gd}$ . The effect on the exact peak value due to the surface barrier pinning is neglected. For  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ ,  $B_{c1}^{ave}$  decreases steadily from 7 G at 2 K to 6 G at 5 K, 4 G at 10 K, and below 1 G at 15 K. A simple empirical parabolic fitting gives  $B_{c1}^{ave}(T) = B_{c1}^{ave}(0)[1 - (T/T_{SVS})^2]$ , with average  $B_{c1}^{ave}(0) \sim 7$  G and spontaneous vortex state temperature  $T_{SVS} = 16$  K. The Ginzburg-Landau anisotropy formula  $B_{c1}^{ave} = (2B_{c1}^{ab} + B_{c1}^c)/3$ , then provides an estimated  $c$ -axis lower critical field  $B_{c1}^c \sim 17$  G and anisotropy parameter  $\sim 8.5$ .

The lower field superconducting phase diagram for the polycrystalline bulk sample is shown in Fig. 4. The average lower critical field  $B_{c1}^{ave}$  separates the Meissner state and vortex state. The upper critical field  $B_{c2}$  and vortex melting field  $B_{\text{melting}}$  determined from magnetoresistivity measurements are field-independent below

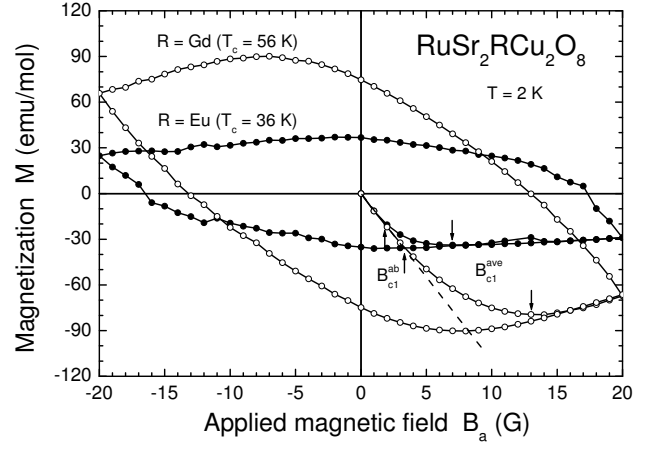


FIG. 3: The low-field superconducting hysteresis loops  $M$ - $B_a$  at 2 K for  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  and  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ . Average lower critical field  $B_{c1}(\text{ave})$  at peak values and  $ab$ -plane  $B_{c1}^{ab}$  for deviation from initial linear lines are indicated by arrows.

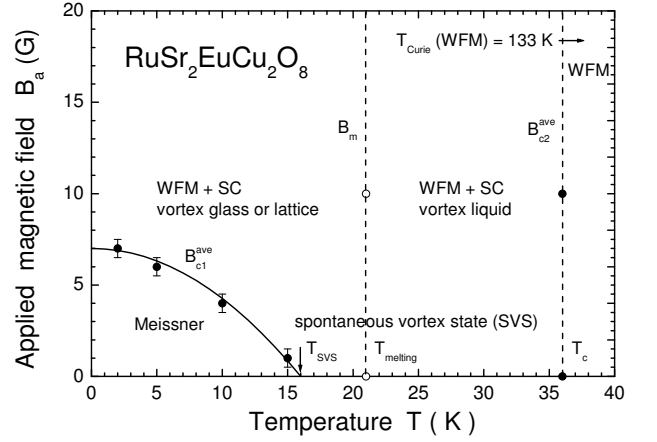


FIG. 4: The low field, low temperature superconducting phase diagram  $B_a(T)$  of  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ . The spontaneous vortex state (SVS) occurs between  $T_{SVS} = 16$  K and  $T_c = 36$  K. Vortex lattice/glass melting temperature  $T_{\text{melting}}$  is defined from temperature at which resistivity drops to zero.

20 G. The WFM-induced internal dipole field  $B_{\text{dipole}}$  of 8.8 G on the  $\text{CuO}_2$  bi-layers is estimated using extrapolated  $B_{c1}^{ave}$  value at  $T = 0$ ,  $(B_{c1}^{ave}(0) + B_{\text{dipole}})/B_{c1}^{ave}(0) = T_c/T_{SVS}$ . It further yields a small net spontaneous magnetic moment  $\mu_s$  of  $0.1 \mu_B$  per Ru, based on the relation of  $B_{\text{dipole}} \sim 2\mu_s/(c/2)^3$ , where  $c/2 = 0.58$  nm is the distance between midpoint of  $\text{CuO}_2$  bi-layers and two nearest-neighbor Ru moments. If the WFM structure is indeed a G-type antiferromagnetic order with  $1.5 \mu_B$  for  $\text{Ru}^{5+}$  in  $t_{2g}$  states canted along the tetragonal basal plane, the small  $\mu_s$  would give a canting angle of  $4^\circ$  from the tetragonal  $c$ -axis and be difficult to be detected in neutron diffraction with a resolution  $\sim 0.1 \mu_B$ .

The molar specific heat data up to 70 K in Fig. 5 show a good agreement between Eu- and Gd-compounds,

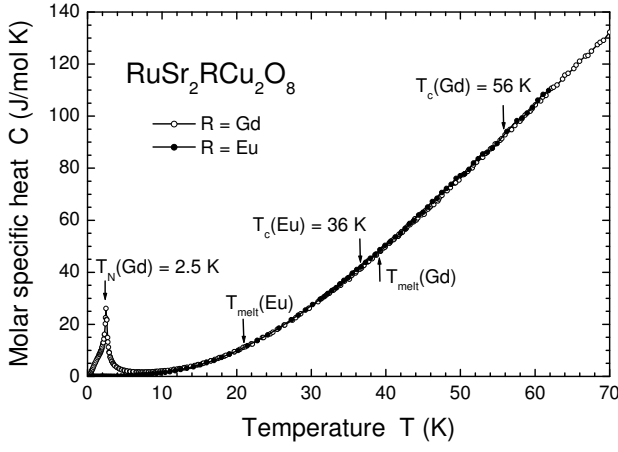


FIG. 5: The molar specific heat of  $\text{RuSr}_2\text{RCu}_2\text{O}_8$  ( $R = \text{Eu}, \text{Gd}$ ). Antiferromagnetic  $\text{Gd}^{3+}$  ordering prevails at 2.5 K.

except that a peak reflects the antiferromagnetic  $\text{Gd}^{3+}$  ordering near  $T_N \sim 2.5$  K. Consistent with previous results for lower- $T_c$  Gd-compounds in zero applied magnetic field.<sup>15,28</sup> No visible jump in specific heat was observed near  $T_c = 36$  K. This is not surprising, since only the electronic component in specific heat would change with superconducting transition, but it is easily overshadowed by the much larger phonon contribution. Specifically, assuming a same magnitude as that observed in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  ( $\Delta C \sim 0.33$  J/mol K at  $T_c = 37$  K) and  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $\Delta C \sim 4.6$  J/mol K at  $T_c = 92$  K),<sup>53</sup> an estimated  $\Delta C \sim 1$  J/mol K at  $T_c$  here is only about 1% of total specific heat, falling below the experimental precision. In addition, the broad resistivity transition due to vortex melting would further points to a correspondingly reduced height of  $\Delta C$ .

It would be of interest to obtain information on the  $\text{Gd}^{3+}$  ordering. To do so, delineation of various contributions to the total specific heat begins with the non-magnetic Eu-compound up to 7 K. In the format of  $C/T$  versus  $T^2$ , the data in Fig. 6 can be well fitted by the sum of four terms with different temperature dependence:

$$C = \beta T^3 + \alpha T^2 + \gamma T + \frac{\eta}{T^2}. \quad (1)$$

The coefficient of the first term,  $\beta = 0.89$  mJ/mol  $\text{K}^4$ , can be used to derive a Debye temperature  $\theta_D$  of the lattice,

$$\beta = n(12\pi^4/5)N_A k/\theta_D^3, \quad (2)$$

where  $N_A$  is Avogadro's number,  $k$  the Boltzmann constant, and the number of atoms per formula unit  $n = 14$ . The  $\theta_D$  value of 312 K thus obtained supports the validity of the  $T^3$ -dependence approximation in Debye model for the lattice specific heat below 7 K  $\sim \theta_D/50$ . The quadratic term has two possible sources: the nodal line excitation for  $d$ -wave pairing symmetry and the spin wave excitation of WFM Ru sublattice. The fact that the

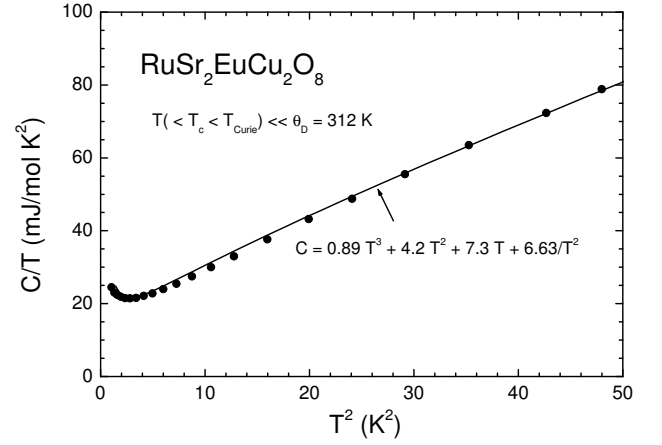


FIG. 6: Low temperature  $C/T$  versus  $T^2$  of  $\text{RuSr}_2\text{EuCu}_2\text{O}_8$  from 1 K to 7 K. Data above 1 K can be fitted using  $C(T) = \beta T^3 + \alpha T^2 + \gamma T + \eta/T^2$  with Debye temperature  $\theta_D = 312$  K.

observed  $\alpha$  value of 4.2 mJ/mol K is much large than 0.1 mJ/mol K of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  could be an indication of a less important nodal line excitation, but an enhanced spin wave excitation. The linear term is considered normally as an electronic contribution, which is not expected to exist in a superconductor at temperature much lower than  $T_c$ . While the observed coefficient  $\gamma = 7.3$  mJ/mol  $\text{K}^2$  is comparable to that of some cuprates, its origin remains to be identified. One plausible explanation is based on the complicated magnetic structure and mixed valence. Such a scenario could lead to a spin glass-like lattice, for which an even larger linear term in specific heat has been observed in another Ru compound of  $\text{Ba}_2\text{PrRuO}_6$ .<sup>54</sup>

The last term with a  $T^{-2}$  dependence is most likely the high-temperature tail of a Schottky anomaly. Its occurrence at the relatively low temperatures suggests nuclear energy splittings being the cause. Such energy splittings occur typically for nuclei having a spin  $I$  and magnetic moment  $\mu_n$  in a hyperfine magnetic field  $H_{hf}$ . For the calorimetric measurements under consideration, they are most likely associated with the Ru nuclei, since the  $4d$  magnetic moments of ordered Ru ions are spatially fixed, polarizing the  $s$ -electrons and producing a net spin at the nuclei, yielding a hyperfine field. There are two Ru isotopes with non-zero  $\mu_n$ :  $^{99}\text{Ru}$  (fractional natural abundance  $A = 0.1276$ ,  $I = 5/2$ , and  $\mu_n = -0.6413$ ) and  $^{101}\text{Ru}$  ( $A = 0.1706$ ,  $I = 5/2$ , and  $\mu_n = -0.7188$ ).<sup>55</sup> However, nuclear energy splittings can also be caused by the interaction between the quadrupole moment of a nucleus and the electric field gradient produced by neighboring atoms. The electric field gradient could be quite high in the layered compound. Meanwhile, Cu and Eu or  $^{155}\text{Gd}$  ( $A = 14.7\%$ ) and  $^{157}\text{Gd}$  ( $A = 15.7\%$ ) nuclei all have non-zero quadrupole moment. Without the full knowledge of magnetic hyperfine field and electric field gradient, it is not feasible at present to delineate the experimentally obtained  $\eta$  of 6.63 mJ/mol into the two different con-

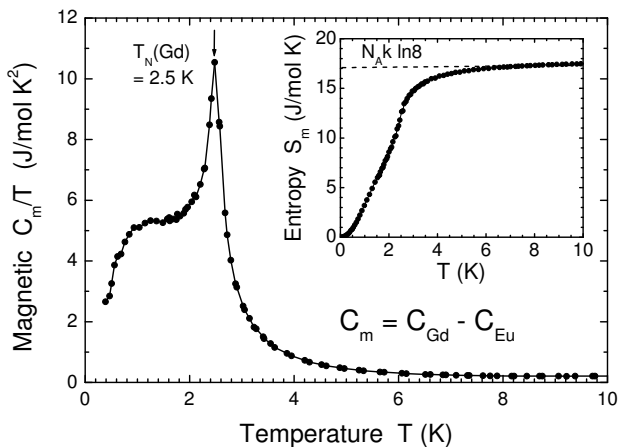


FIG. 7: Temperature dependence of magnetic specific heat and entropy (inset) associated with  $\text{Gd}^{3+}$  ordering in  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ .

tributions.

By assuming that its various coefficients in Eq. (1) for Eu-compound remain the same for the Gd-compound, One can then obtain the magnetic contribution to specific heat associated with antiferromagnetic  $\text{Gd}^{3+}$  ordering as

$$C_m = C_{\text{Gd}} - C_{\text{Eu}}. \quad (3)$$

The results are shown in Fig. 7. Using the format of  $C_m/T$  versus  $T$ . It is of interest to note a broad shoulder below  $T_N$ , a common feature seemingly prevailing in other similar type of compounds such as  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{GdBa}_2\text{Cu}_4\text{O}_8$  and  $\text{TlBa}_2\text{GdCu}_2\text{O}_7$ .<sup>56,57,58</sup> According to Fishman and Liu,<sup>59</sup> it is due to spin fluctuations in the normally ordered state, and such fluctuations are more pronounced for large spins. Indeed,  $\text{Gd}^{3+}$  has the largest spin among all  $\text{R}^{3+}$  ions. The areal integral in Fig. 7, including that associated with the broad shoulder should yield the magnetic entropy,

$$S_m = \int (C_m/T) dT. \quad (4)$$

As shown in the inset,  $S_m$  reaches a saturation value of 17.6 J/mol K around 10 K. Considering the built-in approximation in Eq. (4), it agrees exceptional well with the theoretical value of  $N_A k \ln(2J+1) = N_A k \ln 8 = 17.2$  J/mol K for the complete ordering of  $\text{Gd}^{3+}$ .

#### IV. CONCLUSION

The lower critical field with  $B_{c1}(0) = 7$  G and  $T_{SVS} = 16$  K indicates the existence of a spontaneous vortex state (SVS) between 16 K and  $T_c$  of 36 K. This SVS state is closely related to the weak-ferromagnetic order with a net spontaneous magnetic moment of  $\sim 0.1 \mu_B/\text{Ru}$ , which generates a weak magnetic dipole field around 8.8 G in the  $\text{CuO}_2$  bi-layers. The vortex melting transition temperature at 21 K obtained from resistivity measurements and the onset of diamagnetic signal indicates a broad vortex liquid region due to the coexistence and interplay between superconductivity and WFM order. No visible specific heat jump was observed near  $T_c$  for Eu- and Gd-compound, since the electronic specific heat is easily overshadowed by the large phonon contributions and the expected jump would spread over a wide range of temperature due to vortex melting. Finally, the magnetic entropy associated with  $\text{Gd}^{3+}$  antiferromagnetic ordering at 2.5 K is confirmed to be close to  $N_A k \ln 8$  for  $J = S = 7/2$ .

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